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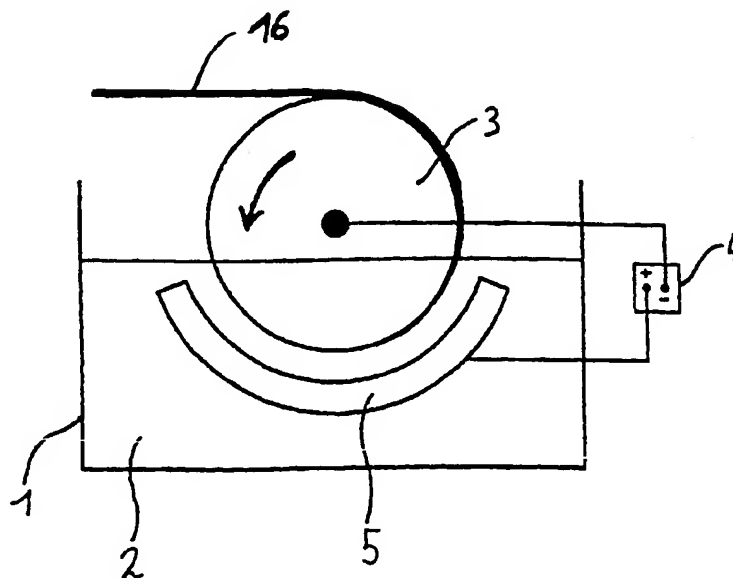
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(54) Title: PROCESS FOR ELECTROPLATING METALLIC AND METALL MATRIX COMPOSITE FOILS, COATINGS AND MICROCOMPONENTS



(57) Abstract: The invention relates to a process for forming coatings or free-standing deposits of nano-crystalline metals, metal alloys or metal matrix composites. The process employs drum plating or selective plating processes involving pulse electrode-position and a non-stationary anode or cathode. Novel nano-crystalline metal matrix composites and micro components are disclosed as well. Also described is a process for forming micro-components with grain sizes below 1,000nm.



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**Process For Electroplating Metallic and Metall Matrix Composite Foils,
Coatings and Microcomponents**

5 Field of the Invention

The invention relates to a process for forming coatings of pure metals, metal alloys or metal matrix composites on a work piece which is electrically conductive or contains an electrically conductive surface layer or forming free-standing deposits of nano-crystalline metals, metal alloys or metal matrix composites by employing pulse electrodeposition. The process employs a drum plating process for the continuous production of nanocrystalline foils of pure metals, metal alloys or metal matrix composites or a selective plating (brush plating) process, the processes involving pulse electrodeposition and a non-stationary anode or cathode. Novel nano-crystalline metal matrix composites are disclosed as well. The invention also relates to a pulse plating process for the fabrication or coating of micro-components. The invention also relates to micro-components with grain sizes below 1,000nm.

The novel process can be applied to establish wear resistant coatings and foils of pure metals or alloys of metals selected from the group of Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Pt, Rh, Ru, Sn, V, W and Zn and alloying elements selected from C, P, S and Si and metal matrix composites of pure metals or alloys with particulate additives such as metal powders, metal alloy powders and metal oxide powders of Al, Co, Cu, In, Mg, Ni, Si, Sn, V, and Zn; nitrides of Al, B and Si; C (graphite or diamond); carbides of B, Cr, Bi, Si, W; and organic materials such as PTFE and polymer spheres. The selective plating process is particularly suited for in-situ or field applications such as the repair or the refurbishment of dies and moulds, turbine plates, steam generator tubes, core reactor head penetrations of nuclear power plants and the like. The continuous plating process is particularly suited for pro-

ducing nanocrystalline foils e.g. for magnetic applications. The process can be applied to high strength, equiaxed micro-components for use in electronic, biomedical, telecommunication, automotive, space and consumer applications.

5 Description of Prior Art/Background of the Invention

Nanocrystalline materials, also referred to as ultra-fine grained materials, nanophase materials or nanometer-sized materials exhibiting average grains sizes smaller or equal to 100nm, are known to be synthesized by a number of methods including sputtering, laser ablation, inert gas condensation, high energy ball mill-
10 ing, sol-gel deposition and electrodeposition. Electrodeposition offers the capability to prepare a large number of fully dense metal and metal alloy compositions at high production rates and low capital investment requirements in a single synthesis step.

15

The prior art primarily describes the use of pulse electrodeposition for producing nanocrystalline materials.

Erb in US 5,352,266 (1994) and in US 5,433,797 (1995) describes a process for
20 producing nanocrystalline materials, particularly nanocrystalline nickel. The nanocrystalline material is electrodeposited onto the cathode in an aqueous acidic electrolytic cell by application of a pulsed DC current. The cell also optionally contains stress relievers. Products of the invention include wear resistant coatings, magnetic materials and catalysts for hydrogen evolution.

25

Mori in US 5,496,463 (1996) describes a process and apparatus for composite electroplating a metallic material containing SiC, BN, Si₃N₄, WC, TiC, TiO₂, Al₂O₃, ZnB₃, diamond, CrC, MoS₂, coloring materials, polytetrafluoroethylene

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(PTFE) and microcapsules. The solid particles are introduced in fine form into the electrolyte.

Adler in US 4,240,894 (1980) describes a drum plater for electrodeposited Cu foil
5 production. Cu is plated onto a rotating metal drum that is partially submersed and rotated in a Cu plating solution. The Cu foil is stripped from the drum surface emerging from the electrolyte, which is clad with electroformed Cu. The rotation speed of the drum and the current density are used to adjust the desired thickness of the Cu foil. The Cu foil stripped from the drum surface is subsequently washed
10 and dried and wound into a suitable coil.

Icxi in US 2,961,395 (1960) discloses a process for electroplating an article without the necessity to immerse the surface being treated into a plating tank. The hand-manipulated applicator serves as anode and applies chemical solutions to the
15 metal surface of the work piece to be plated. The work piece to be plated serves as cathode. The hand applicator anode with the wick containing the electrolyte and the work piece cathode are connected to a DC power source to generate a metal coating on the work piece by passing a DC current.

20 Micromechanical systems (MEMS) are machines constructed of small moving and stationary parts having overall dimensions ranging from 1 to 1,000 μ m e.g. for use in electronic, biomedical, telecommunication, automotive, space and consumer technologies.

25 Such components are made e.g. by photo-electroforming, which is an additive process in which powders are deposited in layers to build the desired structure e.g. by laser enhanced electroless plating. Lithography, electroforming and molding (LIGA) and other photolithography related processes are used to overcome aspect

ratio (parts height to width) related problems. Other techniques employed include silicon micromachining, through mask plating and microcontact printing.

3. Summary:

5

It is an object of the invention to provide a reliable and flexible pulse plating process for forming coatings or free-standing deposits of nano-crystalline metals, metal alloys or metal matrix composites.

- 10 It is a further object of the invention to provide micro components with significantly improved property-dependent reliability and improved and tailor-made desired properties for overall performance enhanced microsystems.

15 Preferred embodiments of the invention are defined in the corresponding dependent claims.

The present invention provides a pulse plating process, consisting of a single cathodic on time or multiple cathodic on times of different current densities and single or multiple off times per cycle. Periodic pulse reversal, a bipolar waveform
20 alternating between cathodic pulses and anodic pulses, can optionally be used as well. The anodic pulses can be inserted into the waveform before, after or in between the on pulse and/or before, after or in the off time. The anodic pulse current density is generally equal to or greater than the cathodic current density. The anodic charge (Q_{anodic}) of the "reverse pulse" per cycle is always smaller than the
25 cathodic charge (Q_{cathodic}).

Cathodic pulse on times range from 0.1 to 50 msec (1-50), off times from 0 to 500msec (1-100) and anodic pulse times range from 0 to 50 msec, preferably from 1 to 10msec. The duty cycle, expressed as the cathodic on times divided by the sum of the cathodic on times, the off times and the anodic times, ranges from 5 to 100 %, preferably from 10 to 95 %, and more preferably from 20 to 80 %. The frequency of the cathodic pulses ranges from 1Hz to 1kHz and more preferably from 10Hz to 350Hz.

Nano-crystalline coatings or free-standing deposits of metallic materials were obtained by varying process parameters such as current density, duty cycle, work piece temperature, plating solution temperature, solution circulation rates over a wide range of conditions. The following listing describes suitable operating parameter ranges for practising the invention:

Average current density (if determinable, anodically or cathodically): 0.01 to 20A/cm², preferably 0,1 to 20A/cm², more preferably 1 to 10A/cm²

Duty Cycle 5 to 100%

Frequency: 0 to 1000Hz

Electrolyte solution temperature: - 20 to 85 °C

Electrolyte solution circulation/agitation rates: ≤10 liter per min per cm² anode or cathode area (0.0001 to 10 l/min.cm²)

Work piece temperature: -20 to 45 °C

Anode oscillation rate: 0 to 350 oscillations/min

Anode versus cathode linear speed: 0 to 200 meter/min (brush) 0.003 to 0.16m/min (drum)

The present invention preferably provides a process for plating nanocrisalline metalls, metall matrix composites and microcomponents at deposition rates of at least 0,05 mm/h, preferably at least 0.075 mm/h, and more preferably at least 0,1 mm/h.

5

In the process of the present invention the electrolyte preferably may be agitated by means of pumps, stirrers or ultrasonic agitation at rates of 0 to 750 ml/min/A (ml solution per minute per applied Ampere average current), preferably at rates of 0 to 500 ml/min/A.

10

In the process of the present invention optionally a grain refining agent or a stress relieving agent selected from the group of saccharin, coumarin, sodium lauryl sulfate and thiourea can be added to the electrolyte.

- 15 This invention provides a process for plating nanocrystalline metal matrix composites on a permanent or temporary substrate optionally containing at least 5% by volume particulates, preferably 10% by volume particulates, more preferably 20% by volume particulates, even more preferably 30% by volume particulates and most preferably 40% by volume particulates for applications such as hard
- 20 facings, projectile blunting armor, valve refurbishment, valve and machine tool coatings, energy absorbing armor panels, sound damping systems, connectors on pipe joints e.g. used in oil drilling applications, refurbishment of roller bearing axles in the railroad industry, computer chips, repair of electric motors and generator parts, repair of scores in print rolls using tank, barrel, rack, selective (e.g.
- 25 brush plating) and continuous (e.g. drum plating) plating processes using pulse electrodeposition. The particulates can be selected from the group of metal powders, metal alloy powders and metal oxide powders of Al, Co, Cu, In, Mg, Ni, Si, Sn, V, and Zn; nitrides of Al, B and Si; C (graphite or diamond); carbides of B, Bi, Cr, Si, W; MoS₂; and organic materials such as PTFE and polymer spheres.

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The particulate average particle size is typically below 10 μ m, preferably below 1,000nm (1 μ m), preferably 500nm, and more preferably below 100nm.

The process of this invention optionally provides a process for continuous (drum or belt) plating nanocrystalline foils optionally containing solid particles in suspension selected from metal powders, metal alloy powders and metal oxide powders of Al, Co, Cu, In, Mg, Ni, Si, Sn, V, and Zn; nitrides of Al, B and Si; C (graphite or diamond); carbides of B, Bi, Si, W; MoS₂, and organic materials such as PTFE and polymer spheres to impart desired properties including hardness, wear resistance, lubrication, magnetic properties and the like. The drum or belt provides a temporary substrate from which the plated foil can be easily and continuously removed.

According to a preferred embodiment of the present invention it is also possible to produce nanocrystalline coatings by electroplating without the need to submerge the article to be coated into a plating bath. Brush or tampon plating is a suitable alternative to tank plating, particularly when only a portion of the work piece is to be plated, without the need to mask areas not to be plated. The brush plating apparatus typically employs a soluble or dimensionally stable anode wrapped in an absorbent separator felt to form the anode brush. The brush is rubbed against the surface to be plated in a manual or mechanized mode and electrolyte solution containing ions of the metal or metal alloys to be plated is injected into the separator felt. Optionally, this solution also contains solid particles in suspension selected from metal powders, metal alloy powders and metal oxide powders of Al, Co, Cu, In, Mg, Ni, Si, Sn, V, and Zn; nitrides of Al, B and Si; C (graphite or diamond); carbides of Bi, Si, W; MoS₂; and organic materials such as PTFE and polymer spheres to impart desired properties including hardness, wear resistance, lubrication and the like.

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In the case of drum, belt or brush plating the relative motion between anode and cathode ranges from 0 to 600meters per minute, preferably from 0.003 to 10meters per minute.

- 5 In the process of this invention micro components for micro systems including micro-mechanical systems (MEMS) and micro-optical-systems with grain sizes equal to or smaller than 1,000nm can be produced. The maximum dimension of the microcomponent part is equal to or below 1mm and the ratio between the maximum outside dimension of the microcomponent part and the average grain
10 size is equal to or greater than 10, preferably greater than 100.

The micro components of the present invention preferably may have an equiaxed microstructure throughout the plated component, which is relatively independent of component thickness and structure.

15

It is another aspect of the present invention to provide micro components where the average grain size remains at least an order of magnitude smaller than the external dimensions of the part, thus maintaining a high level of strength.

- 20 The micro components according to this invention have significantly improved property-dependent reliability and improved and tailor-made desired properties of MEMS structures for overall performance enhanced microsystems by preferably equiaxed electrodeposits, eliminating the fine grain to columnar grain transition in the microcomponent, and simultaneously reducing the grain size of the deposits
25 below 1,000nm.

4. Preferred Embodiments of the Invention:

Other features and advantages of of this invention will become more apparent in the following detailed description and examples of preferred embodiments of the invention, together with the accompanying schematic drawings, in which:

5

Figure 1 shows a cross-sectional view of a preferred embodiment of a drum plating apparatus.

Figure 2 shows a cross sectional view of a preferred embodiment of a brush plating apparatus; and

10

Figure 3 shows a plan view of a mechanized motion apparatus for generating a mechanized stroke of the anode brush.

15 Figure 1 schematically shows of a plating tank or vessel (1) filled with an electrolyte (2) containing the ions of the metallic material to be plated. Partially submerged into the electrolyte is the cathode in the form of a rotating drum (3) electrically connected to a power source (4). The drum is rotated by an electric motor (not shown) with a belt drive and the rotation speed is variable. The anode (5) can

20 be a plate or conforming anode, as shown, which is electrically connected to the power source (4). Three different anode dispositions can be used: Conformal anodes, as shown in Figure 1, that follow the contour of the submerged section of the drum (3), vertical anodes positioned at the walls of the tank (1) and horizontal anode positioned on the bottom of the tank (1). In case of a foil (16) of metallic

25 material being electrodeposited on the drum (3), the foil (16) is pulled from the drum surface emerging from the electrolyte (2), which is clad with the electroformed metallic material.

- 10 -

Figure 2 schematically shows a workpiece (6) to be plated, which is connected to the negative outlet of the power source (4). The anode (5) consists of a handle (7) with a conductive anode brush (8). The anode contains channels (9) for supplying the electrolyte solution (2) from a temperature controlled tank (not shown) to the anode wick (absorbent separator) (10). The electrolyte dripping from the absorbent separator (10) is optionally collected in a tray (11) and recirculated to the tank. The absorbent separator (10) containing the electrolyte (2) also electrically insulates the anode brush (8) from the workpiece (6) and adjusts the spacing between anode (5) and cathode (6). The anode brush handle (4) can be moved over the workpiece (6) manually during the plating operation, alternatively, the motion can be motorized as shown in figure 3.

Figure 3 schematically shows a wheel (12) driven by an adjustable speed motor (not shown). A traversing arm (13) can be rotatably attached (rotation axis A) to the rotating wheel (12) at various positions x at a slot (14) with a bushing and a set screw (not shown) to generate a desired stroke. The stroke length can be adjusted by the position x (radius) at which the rotation axis A of traversing arm is mounted at the slot (14). In Figure 3 the traversing arm (13) is shown to be in an no-stroke, neutral position with rotation axis A in the center of the wheel (12). The traversing arm (13) has a second pivot axis B defined by a bearing (not shown), that is slidably mounted in a track (15). As the wheel (12) rotates, the rotation of the traversing arm (13) around axis A at position x causes the traversing arm (13) to reciprocate in the track (15) and to pivot around axis B. An anode (5) having the same features as shown in Fig. 2 is attached to the traversing arm (13) and moves over the workpiece (6) in a motion depending on the position x. Usually the motion has the shape of figure eight. The anode (5) and the workpiece (6) are connected to positive and negative outlets of a power source (not shown), respectively. The cinematic relation is very similar to that of a steam engine.

This invention relies on producing nanocrystalline coatings, foils and microsystem components by pulse electrodeposition. Optionally solid particles are suspended in the electrolyte and are included in the deposit.

- 5 Nanocrystalline coatings for wear resistant applications to date have focused on increasing wear resistance by increasing hardness and decreasing the friction coefficient through grain size reduction below 100nm. It has now been found that incorporating a sufficient volume fraction of hard particles can further enhance the wear resistance of nanocrystalline materials.

10

- The material properties can also be altered by e.g. the incorporation of lubricants (such as MoS₂ and PTFE). Generally, the particulates can be selected from the group of metal powders, metal alloy powders and metal oxide powders of Al, Co, Cu, In, Mg, Ni, Si, Sn, V, and Zn; nitrides of Al, B and Si; C (graphite or diamond); carbides of B, Bi, Si, W; MoS₂; and organic materials such as PTFE and polymer spheres.
- 15

Example 1

- 20 Nanocrystalline NiP-B₄C nanocomposites were deposited onto Ti and mild steel cathodes immersed in a modified Watts bath for nickel using a soluble anode made of a nickel plate and a Dynatronix (Dynanet PDPR 20-30-100) pulse power supply. The following conditions were used:

- 25 Anode/anode area: soluble anode: Ni plate, 80cm²

Cathode/cathode area: Ti or mild steel sheet/appr. 5cm²

Cathode: fixed

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Anode: fixed

Anode versus cathode linear speed: N/A

Average cathodic current density: 0.06 A/cm^2

$t_{\text{on}}/t_{\text{off}}$: 2msec/ 6msec

5 Frequency: 125Hz

Duty Cycle: 25%

Deposition time: 1 hour

Deposition Rate: 0.09mm/hr

Electrolyte temperature: 60°C

10 Electrolyte circulation rate: vigorous agitation (two direction mechanical impeller)

Basic Electrolyte Formulation:

300g/l $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$

45g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$

15 45g/l H_3BO_3

18 g/l H_3PO_4

0.5-3ml/l surfactant to a surface tension of <30dyne/cm

0-2g/l sodium saccharinate

360 g/l boron carbide, 5 μm mean particle diameter

20 pH 1.5-2.5

The hardness values of metal matrix composites possessing a nanocrystalline matrix structure are typically twice as high as conventional coarse-grained metal matrix composites. In addition, the hardness and wear properties of a nanocrystalline

25 NiP-B₄C composite containing 5.9weight% P and 45volume% B₄C are compared with those of pure coarse-grained Ni, pure nanocrystalline Ni and electrodeposited Ni-P of an equivalent chemical composition in the adjacent table. Material hard-

ening is controlled by Hall-Petch grain size strengthening, while abrasive wear resistance is concurrently optimized by the incorporation of B₄C particulate.

Table: NiP-B₄C nanocomposite properties

5

Sample	Grain Size	Vickers Hardness [VHN]	Taber Wear Index [TWI]
Pure Ni	90 μ m	124	37.0
Pure Ni	13 nm	618	20.9
Ni-5.9P	Amorphous	611	26.2
Ni-5.9P-45B ₄ C	12 nm	609	1.5

Example 2

10 Nanocrystalline Co based nanocomposites were deposited onto Ti and mild steel cathodes immersed in a modified Watts bath for cobalt using a soluble anode made of a cobalt plate and a Dynatronix (Dynanet PDPR 20-30-100) pulse power supply. The following conditions were used:

Anode/anode area: soluble anode (Co plate)/ 80cm²

15 Cathode/cathode area: Ti (or mild steel) sheet/appr. 6.5cm²

Cathode: fixed

Anode: fixed

Anode versus cathode linear speed: N/A

Peak cathodic current density: 0.100A/cm²

20 Peak anodic current density: 0.300A/cm²

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Cathodic t_{on} / t_{off} / Anodic t_{on} (t_{anodic}): 16msec / 0msec / 2msec

Frequency: 55.5Hz

Cathodic duty cycle: 89 %

Anodic duty cycle: 11%

5 Deposition time: 1 hour

Deposition Rate: 0.08mm/hr

Electrolyte temperature: 60°C

Electrolyte circulation rate: 0.15liter/min/cm² cathode area (no pump flow; agitation)

10

Electrolyte Formulation:

300 g/l CoSO₄·7H₂O

45 g/l CoCl₂·6H₂O

45 g/l H₃BO₃

15 2 g/l C₇H₄NO₃Na Sodium Saccharinate

0.1 g/l C₁₂H₂₅O₄Na Sodium Lauryl Sulfonate (SLS)

100 g/l SiC, <1μm mean particle diameter

pH 2.5

20 In the adjacent table, the hardness and wear properties of a nanocrystalline Co-SiC composite containing 22volume% SiC are compared with those of pure coarse-grained Co and pure nanocrystalline Co. Hall-Petch grain size strengthening controls material hardening, while abrasive wear resistance is concurrently optimized by the incorporation of SiC particulate.

25

Table: Co nanocomposite properties

Sample	Grain Size	Vickers Hardness [VHN]	Taber Wear Index [TWI]
Pure Co	5 μm	270	32.0
Pure Co	14 nm	538	38.0
Co-22SiC	15 nm	529	7.1

Continuous plating to produce foils e.g. using drum plating nanocrystalline foils optionally containing solid particles in suspension selected from pure metals or alloys with particulate additives such as metal powders, metal alloy powders and metal oxide powders of Al, Co, Cu, In, Mg, Ni, Si, Sn, V, and Zn; nitrides of Al, B and Si; C (graphite or diamond); carbides of B, Bi, Si, W; and organic materials such as PTFE and polymer spheres to impart desired properties including hardness, wear resistance, lubrication, magnetic properties and the like has been accomplished. Nanocrystalline metal foils were deposited on a rotating Ti drum partially immersed in a plating electrolyte. The nanocrystalline foil was electroformed onto the drum cathodically, using a soluble anode made of a titanium container filled with anode metal and using a pulse power supply. For alloy foil production, a stream of the additional cation at a predetermined concentration was continuously added to the electrolyte solution to establish a steady state concentration of alloying cations in solution. For metal and alloy foil production containing matrix composites, a stream of the composite addition was added to the plating bath at a predetermined rate to establish a steady state content of the additive. Three different anode dispositions can be used: Conformal anodes that follow the contour of the submerged section of the drum, vertical anodes positioned at the walls of the vessel and horizontal anode positioned on the bottom of the vessel. Foils were produced at average cathodic current densities ranging from 0.01 to 5A/cm² and preferably from 0.05 to 0.5A/cm². The rotation speed was

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used to adjust the foil thickness and this speed ranged from 0.003 to 0.15rpm (or 20 to 1000cm/hour) and preferably from 0.003 to 0.05rpm (or 20 to 330cm/hour)

Example 3: metal matrix composite drum plating

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Nanocrystalline Co based nanocomposites were deposited onto a rotating Ti drum as described in example 3 immersed in a modified Watts bath for cobalt. The nanocrystalline foil, 15cm wide was electroformed onto the drum cathodically, using a soluble cobalt anode contained in a Ti wire basket and a Dynatronix (Dy-
10 nanet PDPR 20-30-100) pulse power supply. The following conditions were used:

Anode/anode area: conforming soluble anode (Co Pieces in Ti
basket)/undetermined

15 Cathode/cathode area: Ti 600cm²

Cathode: rotating

Anode: fixed

Anode versus cathode linear speed: 0.018rpm

Average Current Density: 0.075A/cm²

20 Peak cathodic current density: 0.150A/cm²

Peak anodic current density: N/A

Cathodic t_{on} / t_{off} / Anodic t_{on} (t_{anodic}): 1msec / 1msec / 0msec

Frequency: 500Hz

Cathodic duty cycle: 50 %

25 Anodic duty cycle: 0%

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Deposition time: 1 hour

Deposition Rate: 0.05 mm/hr

Electrolyte temperature: 65°C

Electrolyte circulation rate: 0.15 liter/min/cm² cathode area (no pump flow;

5 agitation)

Electrolyte Formulation:

300 g/l CoSO₄×7H₂O

45 g/l CoCl₂×6H₂O

10 45 g/l H₃BO₃

2 g/l C₇H₄NO₃SNa Sodium Saccharinate

0.1 g/l C₁₂H₂₅O₄SNa Sodium Lauryl Sulfonate (SLS)

5 g/l Phosphorous Acid

35 g/l SiC, <1 μm mean particle diameter

15 .5 g/l Dispersant

pH 1.5

The Co/P-SiC foil had a grain size of 12 nm, a hardness of 690 VHN, contained 1.5% P and 22 volume% SiC.

20

Example 4

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Nanocrystalline nickel-iron alloy foils were deposited on a rotating Ti drum partially immersed in a modified Watts bath for nickel. The nanocrystalline foil, 15cm wide was electroformed onto the drum cathodically, using a soluble anode made of a titanium wire basket filled with Ni rounds and a Dynatronix (Dynanet PDPR 50-250-750) pulse power supply. The following conditions were used:

Anode/anode area: conforming soluble anode (Ni rounds in a metal cage)/undetermined

Cathode/cathode area: submersed Ti drum/appr. 600cm²

10 Cathode: rotating at 0.018rpm (or 120cm/hour) Anode: fixed

Anode versus cathode linear speed: 120cm/hour

Average cathodic current density: 0.07A/cm²

t_{on}/t_{off}: 2msec/2msec

Frequency: 250Hz

15 Duty Cycle: 50 %

Production run time: 1 day

Deposition Rate: 0.075mm/hr

Electrolyte temperature: 60°C

Electrolyte circulation rate: 0.15liter/min/cm² cathode area

20

Electrolyte Formulation:

260 g/l NiSO₄·7H₂O

45 g/l NiCl₂·6H₂O

12 g/l FeCl₂·4H₂O

25 45 g/l H₃BO₃

46 g/l Sodium Citrate

2 g/l Sodium Saccharinate

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2.2 ml/l NPA-91

pH 2.5

Iron Feed Formulation:

5 81 g/l $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

11 g/l $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$

13 g/l H_3BO_3

9 g/l Sodium Citrate

4 g/L H_2SO_4

10 0.5 g/l Sodium Saccharinate

pH 2.2

rate of addition: 0.3 l/hr

Composition: 23-27 wt.%Fe

15 Average grain size: 15 nm

Hardness: 750Vickers

Selective or brush plating is a portable method of selectively plating localized areas of a work piece without submersing the article into a plating tank. There are significant differences between selective plating and tank and barrel plating applications. In the case of selective plating it is difficult to accurately determine the cathode area and therefore the cathodic current density and/or peak current density is variable and usually unknown. The anodic current density and/or peak current density can be determined, provided that the same anode area is utilized during the plating operation, e.g. in the case of flat anodes. In the case of shaped anodes the anode area can not be accurately determined e.g. in the case of a shaped anode

and a shaped cathode the "effective" anode area also changes during the plating operation. Selective plating is performed by moving the anode, which is covered with the absorbent separator wick and containing the electrolyte, back and forth over the work piece, which is typically performed by an operator until the desired overall area is coated to the required thickness.

Selective plating techniques are particularly suited for repairing or refurbishing articles because brush plating set-ups are portable, easy to operate and do not require the disassembly of the system containing the work piece to be plated. Brush plating also allows plating of parts too large for immersion into plating tanks. Brush plating is used to provide coatings for improved corrosion resistance, improved wear, improved appearance (decorative plating) and can be used to salvage worn or mismachined parts. Brush plating systems and plating solutions are commercially available e.g. from Sifco Selective Plating, Cleveland, Ohio, which also provides mechanized and/or automated tooling for use in high volume production work. The plating tools used comprise the anode (DSA or soluble), covered with an absorbent, electrically non-conductive material and an insulated handle. In the case of DSA anodes, anodes are typically made of graphite or Pt-clad titanium and may contain means for regulating the temperature by means of a heat exchanger system. For instance, the electrolyte used can be heated or cooled and passed through the anode to maintain the desired temperature range. The absorbent separator material contains and distributes the electrolyte solution between the anode and the work piece (cathode), prevents shorts between anode and cathode and brushes against the surface of the area being plated. This mechanical rubbing or brushing motion imparted to the work piece during the plating process influences the quality and the surface finish of the coating and enables fast plating rates. Selective plating electrolytes are formulated to produce acceptable coatings in a wide temperature range ranging from as low as -20°C to 85°C . As the work piece is frequently large in comparison to the area being coated selective plating is often applied to the work piece at ambient temperatures, ranging from as low as -20°C

to as high as 45°C. Unlike "typical" electroplating operations, in the case of selective plating the temperature of the anode, cathode and electrolyte can vary substantially. Salting out of electrolyte constituents can occur at low temperatures and the electrolyte may have to be periodically or continuously reheated to dissolve all precipitated chemicals.

A Sifco brush plating unit (model 3030 – 30A max) was set up. The graphite anode tip was inserted into a cotton pouch separator and either attached to a mechanized traversing arm in order to generate the "brushing motion" or moved by an operator by hand back and forth over the work piece, or as otherwise indicated. The anode assembly was soaked in the plating solution and the coating was deposited by brushing the plating tool against the cathodically charged work area that was composed of different substrates. A peristaltic pump was used to feed the electrolyte at predetermined rates into the brush plating tool. The electrolyte was allowed to drip off the work piece into a tray that also served as a "plating solution reservoir" from which it was recirculated into the electrolyte tank. The anode had flow-through holes/channels in the bottom surface to ensure good electrolyte distribution and electrolyte/work piece contact. The anode was fixed to a traversing arm and the cyclic motion was adjusted to allow uniform strokes of the anode against the substrate surface. The rotation speed was adjusted to increase or decrease the relative anode/cathode movement speed as well as the anode/substrate contact time at any one particular location. Brush plating was normally carried out at a rate of approximately 35-175 oscillations per minute, with a rate of 50-85 oscillations per minute being optimal. Electrical contacts were made on the brush handle (anode) and directly on the work piece (cathode). Coatings were deposited onto a number of substrates, including copper, 1018 low carbon steel, 4130 high carbon steel, 304 stainless steel, a 2.5in OD steel pipe and a weldclad I625 pipe. The cathode size was 8cm², except for the 2.5in OD steel pipe where a strip 3cm wide around the outside diameter was exposed and the weldclad I625 pipe on which a defect repair procedure was performed.

A Dynatronix programmable pulse plating power supply (Dynanet PDPR 20-30-100) was employed.

- 5 Standard substrate cleaning and activation procedures provided by Sifco were used.

Example 5:

- 10 Nanocrystalline pure nickel was deposited onto an 8cm^2 area cathode with a 35cm^2 anode using the set-up described. Usually, the work piece has a substantially larger area than the anode. In this example a work piece (cathode) was selected to be substantially smaller than the anode to ensure that the oversized anode, although being constantly kept in motion, always covered the entire work
- 15 piece to enable the determination of the cathodic current density. As a non-consumable anode was used, NiCO_3 was periodically added to the plating bath to maintain the desired Ni^{2+} concentration. The following conditions were used:

Anode/anode area: graphite/ 35cm^2

- 20 Cathode/cathode area: mild steel/ 8cm^2

Cathode: stationary

Anode: oscillating mechanically automated at 50 oscillations per minute

Anode versus cathode linear speed: 125cm/min

Average cathodic current density: 0.2A/cm^2

- 25 $t_{\text{on}}/t_{\text{off}}$: $8\text{msec}/2\text{msec}$

Frequency: 100 Hz

- 23 -

Duty Cycle: 80%,

Deposition time: 1 hour

Deposition rate: 0.125mm/hr

5 Electrolyte temperature: 60°C

Electrolyte circulation rate: 10ml solution per min per cm² anode area or 220ml solution per min per Ampere average current applied

Electrolyte Formulation:

300 g/l NiSO₄·7H₂O

10 45 g/l NiCl₂·6H₂O

45 g/l H₃BO₃

2 g/l Sodium Saccharinate

3 ml/l NPA-91

pH: 2.5

15

Average grain size: 19nm

Hardness: 600Vickers

Example 6:

20

Nanocrystalline Co was deposited using the same set up described under the following conditions:

Anode/anode area: graphite/35cm²

- 24 -

Cathode/cathode area: mild steel/8cm²

Cathode: stationary

Anode: oscillating mechanically automated at 50 oscillations per minute

Anode versus cathode linear speed: 125cm/min

5 Average cathodic current density: 0.10A/cm²

t_{on}/t_{off}: 2msec/6msec

Frequency: 125Hz

Duty Cycle: 25%

Deposition time: 1 hour

10 Deposition rate: 0.05mm/hr

Electrolyte temperature: 65°C

Electrolyte circulation rate: 10 mL solution per min per cm² anode area or 440 ml solution per min per Ampere average current applied

15

Electrolyte Formulation:

300 g/L CoSO₄·7H₂O

45 g/L CoCl₂·6H₂O

45 g/L H₃BO₃

20 2 g/L C₇H₄NO₃Na Sodium Saccharinate

0.1 g/L C₁₂H₂₅O₄Na Sodium Lauryl Sulfonate (SLS)

pH 2.5

Average grain size: 13nm

Hardness: 600Vickers

- 25 -

Example 7:

Nanocrystalline Ni/20%Fe was deposited using the set up described before. A
5 1.5in wide band was plated on the OD of a 2.5in pipe by rotating the pipe along
its longitudinal axis while maintaining a fixed anode under the following conditions:

Anode/anode area/effective anode area: graphite/35cm²/undetermined

10 Cathode/cathode area: 2.5inch OD steel pipe made of 210A1 carbon
steel/undetermined

Cathode: rotating at 12 rpm

Anode: stationary

Cathode versus Anode linear speed: 20cm/min

15 Average cathodic current density: undetermined;

Total current applied: 3.5A

t_{on}/t_{off} : 2msec/6msec

Frequency: 125Hz

Duty Cycle: 25%

20 Deposition time: 1 hour

Deposition rate: 0.05mm/hr

Electrolyte temperature: 55°C

Electrolyte circulation rate: 0.44 liter solution per min per Ampere applied

- 26 -

Electrolyte Formulation:

260 g/l $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 45 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 7.8 g/l $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ 5 45 g/l H_3BO_3 30 g/l $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, Sodium Citrate

2 g/l Sodium Saccharinate

1 ml/l NPA-91

pH 3.0

10

Average grain size: 15 nm

Hardness: 750Vickers

Example 8:

15

A defect (groove) in a weldclad pipe section was filled in with nanocrystalline Ni using the same set up as in Example 1. The groove was about 4.5cm long, 0.5cm wide and had an average depth of approximately 0.175mm, although the rough finish of the defect made it impossible to determine its exact surface area. The area surrounding the defect was masked off and nano Ni was plated onto the de-

20 fective area until its original thickness was reestablished.

Anode/anode area: graphite/35cm²

Cathode/cathode area: I625/undetermined

25 Cathode: stationary

- 27 -

Anode: oscillating mechanically automated at 50 oscillations per minute

Anode versus cathode linear speed: 125cm/min

Average cathodic current density: undetermined

t_{on}/t_{off} : 2msec/6msec

5 Frequency: 125Hz

Duty Cycle: 25%

Deposition time: 2hour

Deposition rate: 0.087mm/hr

10 Electrolyte temperature: 55°C

Electrolyte circulation rate: 0.44 liter solution per min per Ampere average current applied

Electrolyte Formulation:

15 300 g/l $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$

45 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$

45 g/l H_3BO_3

2 g/l Sodium Saccharinate

3 ml/l NPA-91

20 pH 3.0

Average grain size: 20nm

Hardness: 600Vickers

Microcomponents, having overall dimensions below 1,000 μ m (1mm), are gaining increasing importance for use in electronic, biomedical, telecommunication, automotive, space and consumer applications. Metallic macro-system components with an overall maximum dimension of 1cm to over 1m containing conventional grain sized materials (1-1,000 μ m) exhibit a ratio between maximum dimension and grain size ranges from 10 to 10⁶. This number reflects the number of grains across the maximum part dimension. When the maximum component size is reduced to below 1mm using conventional grain-sized material, the component can be potentially made of only a few grains or a single grain and the ratio between the maximum micro-component dimension and the grain size ranges approaches 1. In other words, a single or only a few grains stretch across the entire part, which is undesirable. To increase the part reliability of micro-components the ratio between maximum part dimension and grain size ranges must be increased to over 10 through the utilization of a small grained material, as this material class typically exhibits grain size values 10 to 10,000 times smaller than conventional materials.

For conventional LIGA and other plated micro-components, electrodeposition initially starts with a fine grain size at the substrate material. With increasing deposit thickness in the growth direction; however, the transition to columnar grains is normally observed. The thickness of the columnar grains typically ranges from a few to a few tens of micrometers while their lengths can reach hundreds of micrometers. The consequence of such structures is the development of anisotropic properties with increasing deposit thickness and the reaching of a critical thickness in which only a few grains cover the entire cross section of the components with widths below 5 or 10 μ m. A further decrease in component thickness results in a bamboo structure resulting in a significant loss in strength. Therefore the microstructure of electrodeposited micro-components currently in use is entirely incommensurate with property requirements across both the width and thickness of the component on the basis of grain shape and average grain size.

Heretofore, parts made of conventionally grain-sized materials that have been known to suffer from severe reliability problems with respect to mechanical properties such as the Young modulus, yield strength, ultimate tensile strength, fatigue strength and creep behavior have been shown to be extremely sensitive to processing parameters associated with the synthesis of these components. Many of the problems encountered are caused by incommensurate scaling of key microstructural features (i.e. grain size, grain shape, grain orientation) with the external size of the component resulting in unusual property variations normally not observed in macroscopic components of the same material.

Example 9:

Metal micro-spring fingers are used to contact IC chips with high pad count and density and to carry power and signals to and from the chips. The springs provide high pitch compliant electrical contacts for a variety of interconnection structures, including chip scale semiconductor packages, high-density interposer connectors, and probe contactors. The massively parallel interface structures and assemblies enable high speed testing of separated integrated circuit devices affixed to a compliant carrier, and allow test electronics to be located in close proximity to the integrated circuit devices under test.

The micro-spring fingers require high yield strength and ductility. A 25 μm thick layer of nanocrystalline Ni was plated on 500 μm long gold-coated CrMo fingers using the following conditions:

Anode/anode area: Ni/ $4.5 \times 10^{-3} \text{cm}^2$

Cathode/cathode area: Gold Plated CrMo/approximately 1cm^2

- 30 -

Cathode: stationary

Anode: stationary

Anode versus cathode linear speed: 0 cm/min

Average cathodic current density: 50mA/cm²

5 t_{on}/t_{off} : 10msec/20msec

Frequency: 33Hz

Duty Cycle: 33%

Deposition time: 120 minutes

Deposition Rate: 0.05mm/hr

10 Electrolyte temperature: 60°C

Electrolyte circulation rate: None

Electrolyte Formulation:

300 g/l NiSO₄·7H₂O

15 45 g/l NiCl₂·6H₂O

45 g/l H₃BO₃

2 g/l Sodium Saccharinate

3 ml/l NPA-91

pH 3.0

20

Average grain size: 15-20nm

Hardness: 600Vickers

- 31 -

The nano-fingers exhibited a significantly higher contact force when compared to “conventional grain-sized” fingers.

Claims

- 5 1. Process for cathodically electrodepositing a selected metallic material on a permanent or temporary substrate in nanocrystalline form with an average grain size of less than 100 nm using pulse electrodeposition at a deposition rate of at least 0,05 mm/h, comprising:
providing an aqueous electrolyte containing ions of said metallic material,
10 maintaining said electrolyte at a temperature in the range between 0 to 85°C, providing an anode and a cathode in contact with said electrolyte, passing single or multiple D.C. cathodic-current pulses between said anode and said cathode at a cathodic-current pulse frequency in a range of about 0 and 1000 Hz, at pulsed intervals during which said current passes for a
15 t_{on} -time period in the range of about 0,1 to 50 msec and does not pass for a t_{off} -time period in the range of about 0 to 500 msec, and passing single or multiple D.C. anodic-current pulses between said cathode and said anode at intervals during which said current passes for a t_{anodic} -time period in the range of 0 to 50 msec, a duty cycle being in a range of 5 to 100% and a
20 cathodic charge ($Q_{cathodic}$) per interval being always larger than a anodic charge (Q_{anodic}).
2. Process as claimed in claim 1, characterized in that the single or multiple
25 D.C. cathodic-current pulses between said anode and said cathode have a peak current density in the range of about 0,01 to 20 A/cm².
3. Process as claimed in claim 2, characterized in that the peak current density of the cathodic-current pulses is in the range of about 0,1 to 20 A/cm², preferably in the range of about 1 to 10 A/cm².

4. Process as claimed in any of claims 1 to 3, characterized in that said selected metallic material is (a) a pure metal selected from the group consisting of Ag, Au, Cu, Co, Cr, Ni, Fe, Pb, Pd, Pt, Rh, Ru, Sn, V, W, Zn, or (b) an alloy containing at least one of the elements of group (a) and alloying elements selected from the group consisting of C, P, S and Si.
5
5. Process as claimed in any of claims 1 to 4, characterized in that the t_{on} -time period is in the range of about 1 to about 50 msec, the t_{off} -time period is in the range of about 1 to 100 msec and the t_{anodic} -time period is in the range
10 of about 1 to 10 msec.
6. Process as claimed in any of claims 1 to 5, characterized in that the duty cycle preferably is in the range of 10 to 95 %, and more preferably is in the range of 20 to 80 %.
15
7. Process as claimed in any of claims 1 to 6, characterized in that the cathodic-current pulse frequency ranges from 10 Hz to 350 Hz.
8. Process as claimed in any of claims 1 to 7, characterized in that the deposition rate is preferably at least 0,075 mm/h and more preferably at least
20 0,1 mm/h.
9. Process as claimed in any of claims 1 to 9, characterized by agitating the electrolyte at an agitation rate in the range of 0 to 750 ml/min/A, preferably
25 in a range of 0 to 500 ml/min/A.
10. Process as claimed in claim 9, characterized by agitating the electrolyte by means of pumps, stirrers or ultrasonic agitation.
- 30 11. Process as claimed in any of claims 1 to 10, characterized by a relative motion between anode and cathode.

12. Process as claimed in claim 11, characterized in that the speed of the relative motion between anode and cathode ranges from 0 to 600 m/min, preferably from 0,003 to 10 m/min.
- 5 13. Process as claimed in claim 11, characterized in that the relative motion is achieved by rotation of anode and cathode relative to each other.
- 10 14. Process as claimed in claim 13, characterized by a rotational speed of rotation of anode and cathode relative to each other ranging from 0,003 to 0,15 rpm and preferably from 0,003 to 0,05 rpm.
- 15 15. Process as claimed in claim 11 or claim 12, characterized in that the relative motion is achieved by a mechanized motion generating a stroke of the anode and the cathode relative to each other.
16. Process as claimed in claim 11 or 15, characterized in that the anode is wrapped in an absorbent separator.
- 20 17. Process as claimed in any of claims 1 to 16, characterized in that said electrolyte contains a stress relieving agent or a grain refining agent selected from the group of saccharin, coumarin, sodium lauryl sulfate and thiourea.
- 25 18. Process as claimed in any of claims 1 to 17, characterized in that said electrolyte contains particulate additives in suspension selected from pure metal powders, metal alloy powders or metal oxide powders of Al, Co, Cu, In, Ng, Ni, Si, Sn, V and Zn, nitrides of Al, B and Si, carbon C (graphite or diamond), carbides of B, Bi, Si, W, or organic materials such as PTFE and polymers spheres, whereby the electrodeposited metallic material contains
30 at least 5 % of said particulate additives.

19. Process as claimed in claim 18, characterized in that the electrodeposited metallic material contains at least 10 % of said particulate additives.
- 5 20. Process as claimed in claim 18, characterized in that the electrodeposited metallic material contains at least 20 % of said particulate additives.
21. Process as claimed in claim 18, characterized in that the electrodeposited metallic material contains at least 30 % of said particulate additives.
- 10 22. Process as claimed in claim 18, characterized in that said electro deposited metallic material contains at least 40 % of said particulate additives.
- 15 23. Process as claimed in any of claims 18 to 22, characterized in that the particulate additives average particle size is below 10 μm , preferably below 1000 nm, more preferably below 500 nm and most preferably below 100 nm.
- 20 24. Micro component produced by a pulse electrodeposition process, especially produced by a pulse electrodeposition process as claimed in any of claims 1 to 22, having a maximum dimension of 1 mm, an average grain size equal to or smaller than 1000 nm, the ratio between the maximum dimension and the average grain size being greater than 10.
- 25 25. Micro component as claimed in claim 24, characterized in that the ratio between the maximum dimension of the micro component and the average grain size is greater than 100.
- 30 26. Micro component as claimed in claim 24 or 25, characterized by having a equiaxed micro structure.

Fig. 1

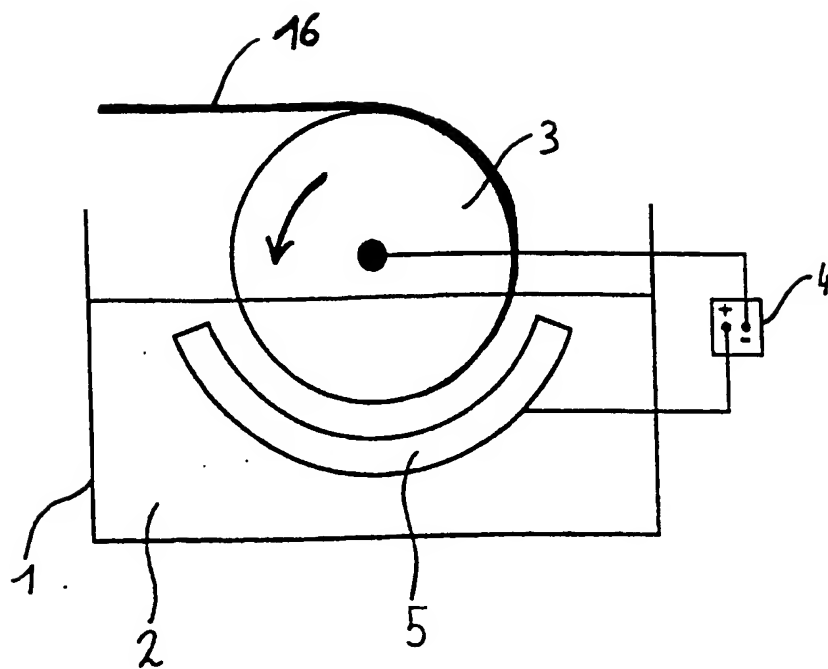
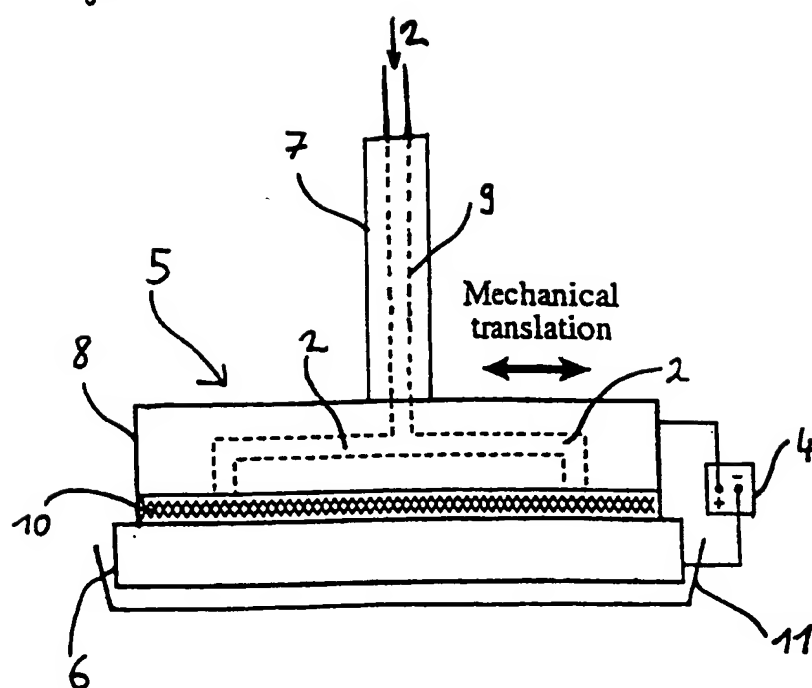
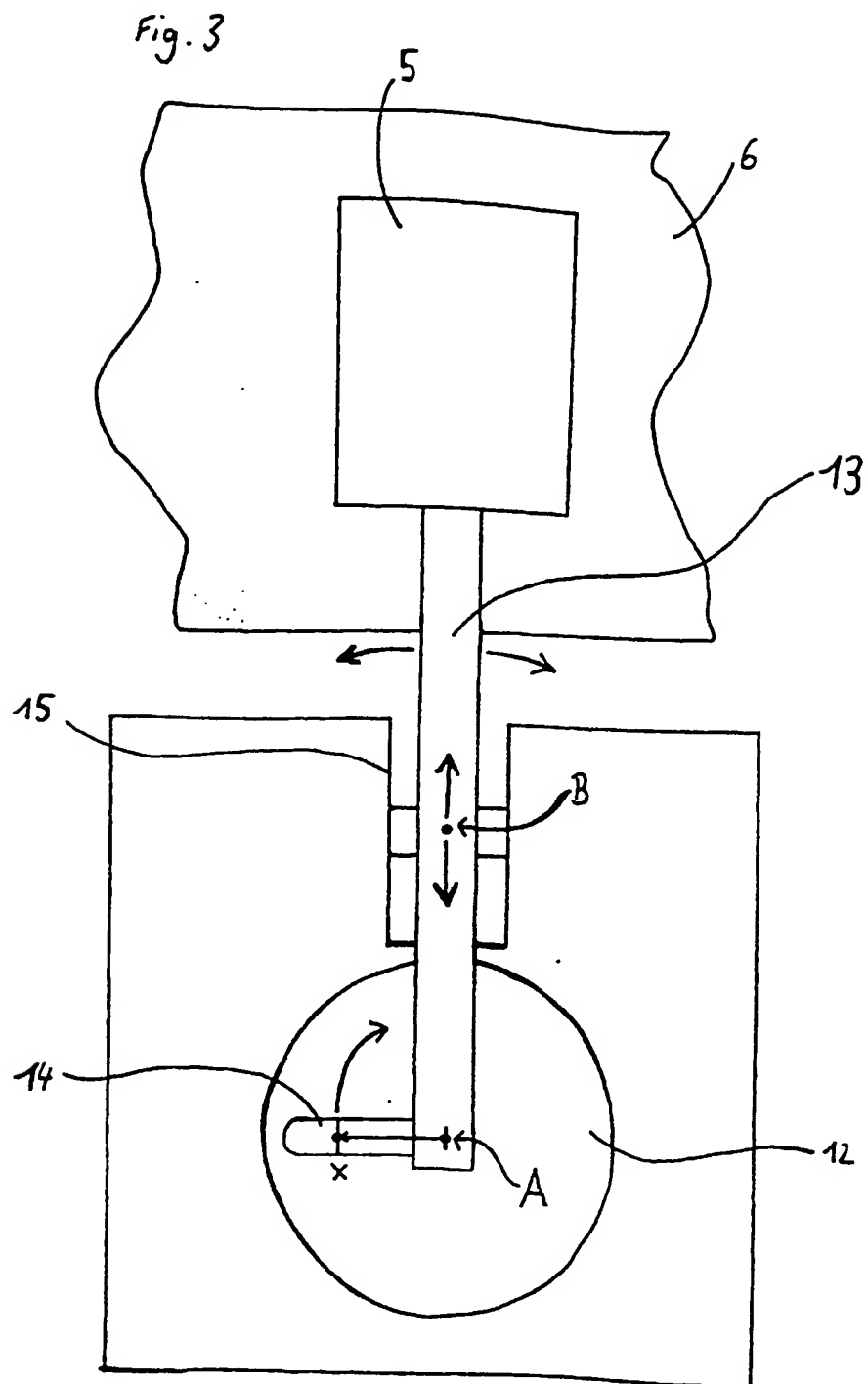


Fig. 2





INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/07023

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C25D1/04 C25D5/02 C25D5/06 C25D5/18 C25D15/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 6 080 504 A (TAYLOR E JENNINGS ET AL) 27 June 2000 (2000-06-27) column 4, line 20 -column 5, line 42 column 8, line 17-22,57-60; figure 1B ---	1,4-7,11
A	GYFTOU P ET AL: "ELECTRODEPOSITION OF NI/SIC COMPOSITES BY PULSE ELECTROLYSIS" TRANSACTIONS OF THE INSTITUTE OF METAL FINISHING, INSTITUTE OF METAL FINISHING. LONDON, GB, vol. 80, no. 3, May 2002 (2002-05), pages 88-91, XP001122455 ISSN: 0020-2967 the whole document --- -/--	1-7,10, 11,13, 18,23

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

17 March 2003

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24/03/2003

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/07023

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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